

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Rec'd PCT/PTO 13 DEC 2004

REC'D 27 APR 2004

WIPO

PCT


Applicant's or agent's file reference 2002CH005	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/B 03/02396	International filing date (day/month/year) 1.1.06.2003	Priority date (day/month/year) 13.06.2002
International Patent Classification (IPC) or both national classification and IPC C09B62/513, C09B62/513		
Applicant CLARIANT INTERNATIONAL LTD et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 34 sheets.

- This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 01.12.2003	Date of completion of this report 23.04.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Weisbrod, T Telephone No. +49 89 2399-8931



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IB 03/02396

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-31 filed with telefax on 06.04.2004

Claims, Numbers

1-6 filed with telefax on 06.04.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/B 03/02396**

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☐ claims Nos.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 1-6 are so unclear that no meaningful opinion could be formed (*specify*):

see separate sheet

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the Standard.

☐ the computer readable form has not been furnished or does not comply with the Standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	3-4
	No: Claims	1,2,5,6
Inventive step (IS)	Yes: Claims	
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-6
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item I

Basis of the opinion

In response to the written opinion the applicant has filed amended pages 1-31 of the description and amended claims 1-6. On pages 2 and 4 of the description as well as in claims 1 and 2 the erroneous values " $\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ " for X_1/X_2 respectively Z_1/Z_2 have been replaced with $\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$. Basis for this correction is found in the reaction schemes on pages 6 and 8. Furthermore, Z_1 and Z_2 in claims 1 and 2 have been replaced with X_1/X_2 for the sake of consistency between the description and the claims. The said amendments are allowable under Article 34(2)(b) PCT and Rule 91.1 PCT.

However, no basis can be found in the application as filed for the replacement of the value SO_3H with OSO_3H for Y on amended page 13, line 3. Consequently, this amendment does not comply with the requirements of Article 34(2)(b) PCT and the IPER has been established as if this amendment had not been made.

The application is directed to

- (i) mixtures containing disazo dyes (1), characterized in that the fraction of the dye (1d) in the mixtures as per formula (1) is more than 40% (claims 1-2),
- (ii) the use of such mixtures as a blue component in the trichromatic dyeing process (claim 3),
- (iii) ink jet printing inks comprising the said mixtures (claim 4),
- (iv) a printing or dyeing process involving such mixtures (claim 5), and
- (v) hydroxyl- or nitrogen-containing organic substrates printed or dyed with the said mixtures (claim 6).

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

In view of the clarity and novelty objections raised under the items V.1.1 and V.3 below, an assessment of the present application with regard to the criterium of inventive step has not been possible.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IB 03/02396

1 Deficiencies of the Application under Article 6 PCT

- 1.1 Present claims 1 and 2 leave the reader in doubt whether the percentage values characterizing the fractions of the compounds 1d, 2, and 3 of the claimed mixtures represent weight, volume, or mole percentage values. Consequently, the subject matter of claims 1 and 2 is not clearly defined. In this context it is noted that the application does not provide an unambiguous definition which kind of percentage values are meant in the claims, such that it appears impossible to render the claims clear in the light of the application as filed. This applies also for the passage on page 8, lines 3-4, which cannot serve as an unambiguous basis that the percentage values in claims 1 and 2 mean mole percentage values and nothing else. Furthermore, it is noted that an unclear definition cannot be allowed in a claim if the definition is essential having regard to the invention. Equally, an unclear definition cannot be used to distinguish the claimed matter from the prior art (cf. item V.3 below concerning document D1).
- 1.2 In addition, the statement that any reference to compounds and mixtures in the plural shall also be construed as a reference to a compound or mixture in the singular (the application, page 4) implies that claims 1 and 2 are also directed to compound 1d per se rather than to mixtures as defined in the claims. This inconsistency between description and claims adds to the unclarity of the claims.

2 Reference is made to the following documents.

D1: CH-A-657 865, 30.09.1986; cited in the application.
D2: DE-A-195 23 245, 02.01.1997.
D3: CH 302 016, 01.12.1954.
D4: US-A-4 911 735, 27.03.1990; cited in the application.
D5: Fachlexikon ABC Chemie, Band 2, 1987, 1206: "Wasserglas".
D6: Roempp Internet-Edition, "Wasserglas".

D5 and D6 were introduced by the applicant during the procedure.

3 Novelty

In view of D1 the present claims 1, 2, 5, and 6 do not comply with the criterion of novelty according to Article 33(2) PCT.

D1 relates to reactive disazo dyes such as the dye according to example 1 (page 5; identical with present compound 1a), their use in dyeing processes of hydroxyl-containing organic substrates, as well as the dyed substrates. According to the present application the addition of 1.5 to 2.4 equivalents of a strong base (e.g. sodium hydroxide) to the dye of example 1 according to D1 produces mixtures with 1d as the main component as claimed in the present claims 1 and 2 (cf. present application, page 7, lines 14-17; page 8, lines 3-4; and page 16, examples 1 and 2). Similarly, the document D1 discloses already a colouration procedure (page 7; "Färbevorschrift V") wherein 6 parts of the said dye of example 1 is treated with 50 parts of a solution comprising 16 g of sodium hydroxide per litre. Such mixture contains 3.28 mol sodium hydroxide per mol of dye, i.e. 1.64 equivalents of sodium hydroxide based on the dye, and is thus considered to produce a mixture according to the present claims 1 and 2 (note that according to page 16 of the present application 1.5 respectively 2 equivalents of sodium hydroxide result in mixtures containing about 36 parts respectively about 77 parts of 1d). The subject matter of the present claims 1, 2, 5, and 6 is thus considered to lack novelty in view of D1, unless the applicant was able to provide substantiated evidence that the alkaline dye mixture according to "Färbevorschrift V" of D1 does not fall under the scope of the present claims 1 and 2. The mere fact that in the "Färbevorschrift V" of D1 a certain amount of "Wasserglas" is present besides the sodium hydroxide does not per se render the claimed matter novel over D1, unless this was substantiated by an appropriate comparison test (however, in this respect the applicant's attention is again drawn to the fact that the exact composition of the claimed mixture is not clearly defined in the present claims 1 and 2; cf. item 1.1 above).

D2 and **D3** relate to disazo reactive dyes but do not disclose the present compound 1d or mixtures containing this compound. The documents do thus not appear relevant to the question of novelty of the present application.

D4 relates to a dyeing process with a trichromatic dyeing recipe wherein at least one of the dyes reacts with the fibre via a vinyl sulfonyl radical. The document does not appear relevant to the question of novelty of the present claimed matter, because mixtures containing the present dye 1d are not explicitly disclosed in this document.

D5 and **D6** relate to "Wasserglas" and its properties. These documents are irrelevant to the question of novelty of the application.

case 2002CH005 (corrected according to R 91.1 PCT)

1

Dyes having adapted affinity

This invention relates to reactive dye mixtures, their preparation and use for dyeing or printing fibre materials, including in particular by ink jet processes. The invention
5 further relates to dye mixtures for the trichromatic dyeing process containing the novel reactive dye mixtures and processes for their use.

Trichromatic dyeing is well known from the literature for different classes of dye, for example from EP 83 299, DE 2623178, EP 226 982 and EP 808 940.

10

The dyeing and printing of cotton and cellulosic materials requires dyes or dye mixtures which have an adapted affinity and which also provide good wash-off with regard to unfixed portions. They shall further possess a high reactivity, so that only brief dwell times are needed, and they shall provide in particular dyeings having high degrees of
15 fixation.

20

The novel dyes should be notable in particular for high fixation yields and high fibre-dye bond stabilities and, moreover, portions not fixed to the fibre should be easy to wash off.

They should further provide dyeings having good all-round fastnesses, for example light and wet fastnesses.

25

The dyes to be used in the process shall exhibit a uniform colour build-up in a constant hue at various concentrations.

30

Reactive dyes having two (or more) sulphatoethyl sulphone reactive groups that, in an exhaust process, have little affinity for fibre before alkali is added but will suddenly go onto the fibre after alkali has been added may lead to sketchy or unlevel dyeings in the exhaust process. Such dyes are difficult to combine in trichromatic dyeings with further trichromatic partners of medium and high affinity.

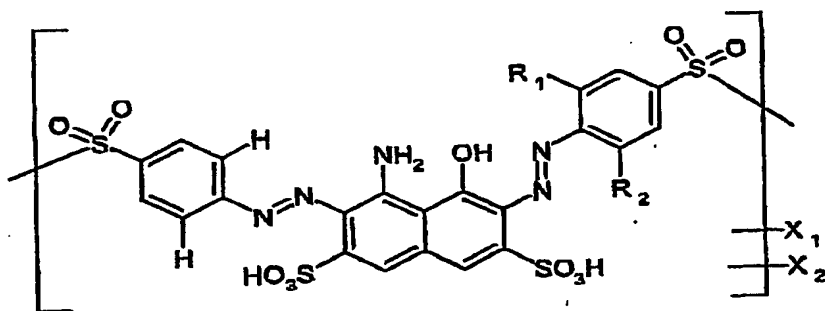
case 2002CH005 (corrected according to R 91.1 PCT)

2

The present invention therefore had for its object to find novel, improved reactive dyes or reactive dye mixtures which possess the above-characterized qualities to a high degree.

- 5 It has been determined that the mixtures according to the invention, of defined novel bireactive dye mixtures, achieve the stated object.

The invention accordingly provides mixtures containing compounds of formula 1



1

- 10 or mixtures of compounds of formula 1
where

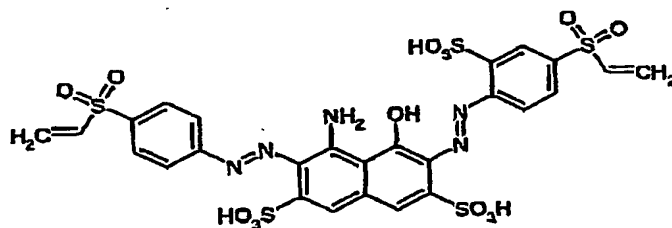
R_1 is H, SO_3H ,

R_2 is H, SO_3H

X_1 is $CH=CH_2$, $CH_2CH_2OSO_3H$

15 X_2 is $CH=CH_2$, $CH_2CH_2OSO_3H$,

characterized in that the fraction of the compound 1d



1d

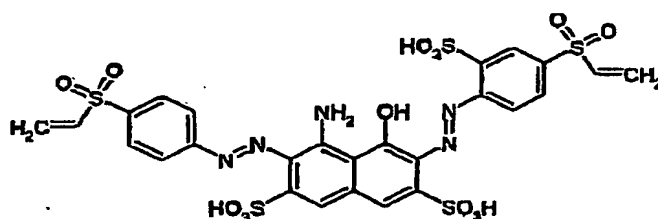
- 20 in the mixtures as per formula 1 is more than 40 %.

case 2002CH005 (corrected according to R 91.1 PCT)

3

Dye 1 according to the invention and mixtures of such dyes are suitable as a blue component for the trichromatic dyeing process. The dye 1d according to the invention is particularly suitable as blue components for the trichromatic dyeing process.

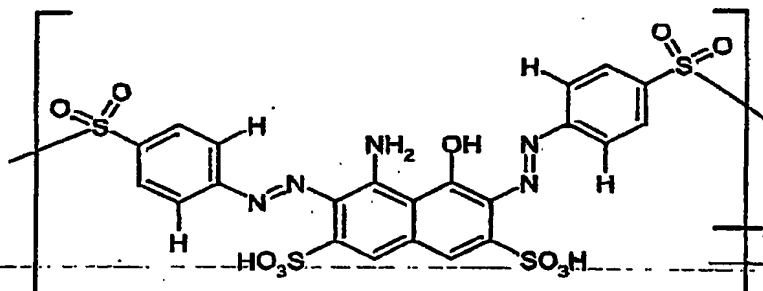
- 5 Preferred mixtures containing mixtures of compounds as per formula 1 the mixture of the compounds as per formula 1 comprises more than 50% of the compound as per formula 1d



1d

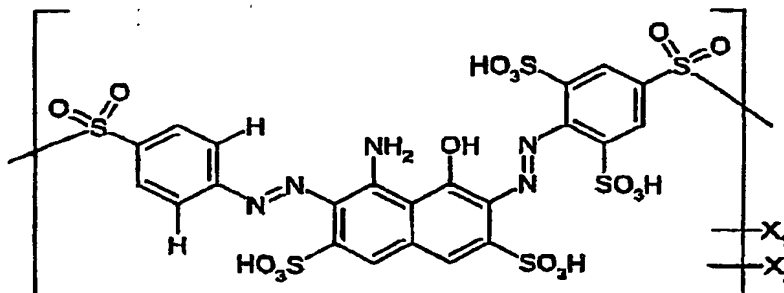
10

and less than 20% of the compound as per formula 2



2

and less than 10% of the compound as per formula 3



3

15

case 2002CH005 (corrected according to R 91.1 PCT)

4

where

R₁ is H, SO₃H,

R₂ is H, SO₃H

X₁ is CH=CH₂, CH₂CH₂OSO₃H

5 X₂ is CH=CH₂, CH₂CH₂OSO₃H.

Dye mixtures suitable for dyeing by the trichromatic process contain dyes as per the formula 1 as blue elements together with at least one red or reddish brown dyeing component and at least one yellow or orange dyeing component.

10

The inventive compounds and mixtures of compounds are suitable for dyeing or printing hydroxyl- or nitrogen-containing organic substrates.

15

As per another aspect of the invention there is accordingly provided a process for dyeing or printing hydroxyl- or nitrogen-containing organic substrates wherein dyeing or printing is carried out with the above-defined compounds or mixtures.

20

It should be noted that any reference to compounds or mixtures in the plural shall also be construed as a reference to a compound or a mixture in the singular, and vice versa. Any reference to printing techniques always comprehends as well as the classic processes the more recent printing processes such as for example the ink jet printing process.

25

Preferred substrates are leather and fibre materials which comprise natural or synthetic polyamides and especially natural or regenerated cellulose, such as cotton, filament viscose or staple viscose. The most preferred substrate is textile material comprising cotton.

30

As per another aspect of the present invention there is provided for the use of the above-defined compounds, their salts or mixtures for dyeing or printing the above-described substrates.

case 2002CH005 (corrected according to R 91.1 PCT)

5

The compounds of the formula 1 can be used in dyeing liquors or in print pastes according to all dyeing or printing processes customary for reactive dyes. Preference is given to dyeing by the exhaust process in the temperature range of 40-70°C.

- 5 The compounds as per the invention can be used as individual dyes or, on account of their good compatibility, also as a combination element with other reactive dyes of the same class which possess comparable dyeing properties, such as for example their general fastnesses, their exhaustion and fixation yield, etc. The combination-shade dyeings obtained are as fast as the dyeings with the individual dye. Especially the dyes
- 10 of the formula 1 are suitable as a blue trichromatic element.

- The compounds of the formula 1 give good exhaustion and fixation yields. The unfixed dye portion is readily washed off. The dyeings and prints obtained exhibit good light fastness. They additionally exhibit good wet fastness properties for example with regard
- 15 to washing, water, seawater and perspiration fastness and have good stability to oxidative influences such as to chlorinated water, hypochlorite bleach, peroxide bleach and also to perborate- and percarbonate-containing laundry detergents including especially those containing bleach activators, such as TAED etc.

- 20 As per a further aspect of the present invention there is provided a hydroxyl- or nitrogen-containing organic substrate which has been dyed or printed as per the above-described dyeing or printing process, including the ink jet printing process.

- The present invention likewise provides substrates, especially cellulose, polyamides and
- 25 animal fibres, preferably cotton, that have been dyed with such compounds.

- The invention likewise provides for the use of a compound of the formula (I) or mixtures thereof as a component in an ink jet printing ink. The invention further provides ink jet printing inks comprising mixtures according to the formula (I) or
- 30 mixtures thereof. Such printing inks can be produced using various organic solvents and their mixtures, such as for example alcohols, ethers, esters, nitriles, carboxamides, cyclic amides, urea, sulphones and sulphone oxides.

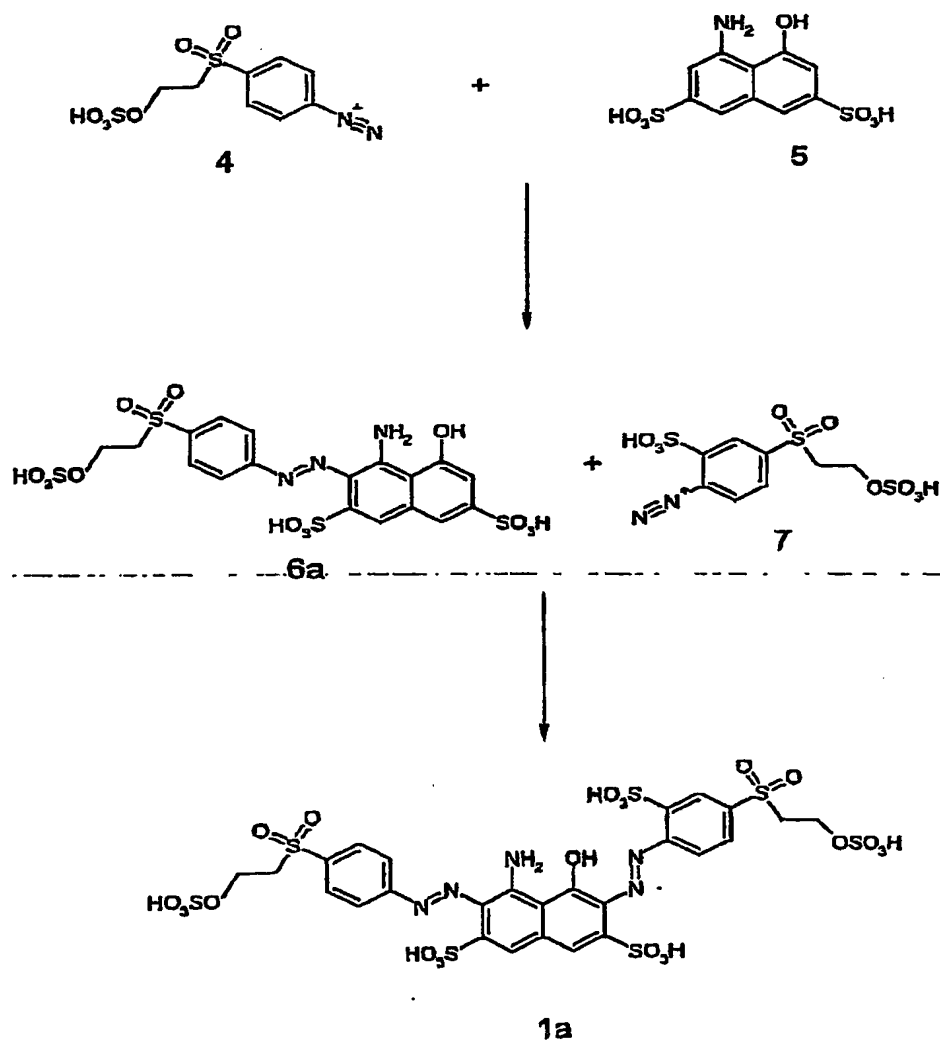
case 2002CH005 (corrected according to R 91.1 PCT)

6

Ink jet inks generally contain in total 0.5 to 35% by weight and preferably 1.5 to 15% by weight (reckoned dry) of one or more of the compounds according to the invention.

The process for producing the dye mixtures as per the formula 1 according to the invention comprises the following steps: The diazonium salt (4) is coupled under acid conditions onto 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (5) to form the monoazo dye (6a). The monoazo dye 6a then has the diazonium salt 7 coupled onto it under neutral conditions to form the dye 1a.

10

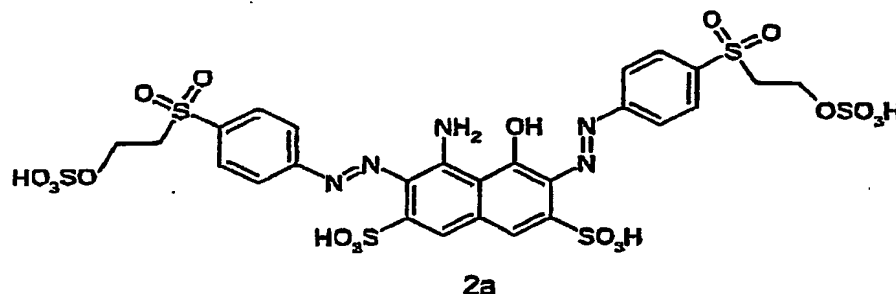


case 2002CH005 (corrected according to R 91.1 PCT)

7

The compound (1a) is the bis-sulphatoethylsulphonyl reactive dye described in Example 1 of the patent specification CH 657 865 A5.

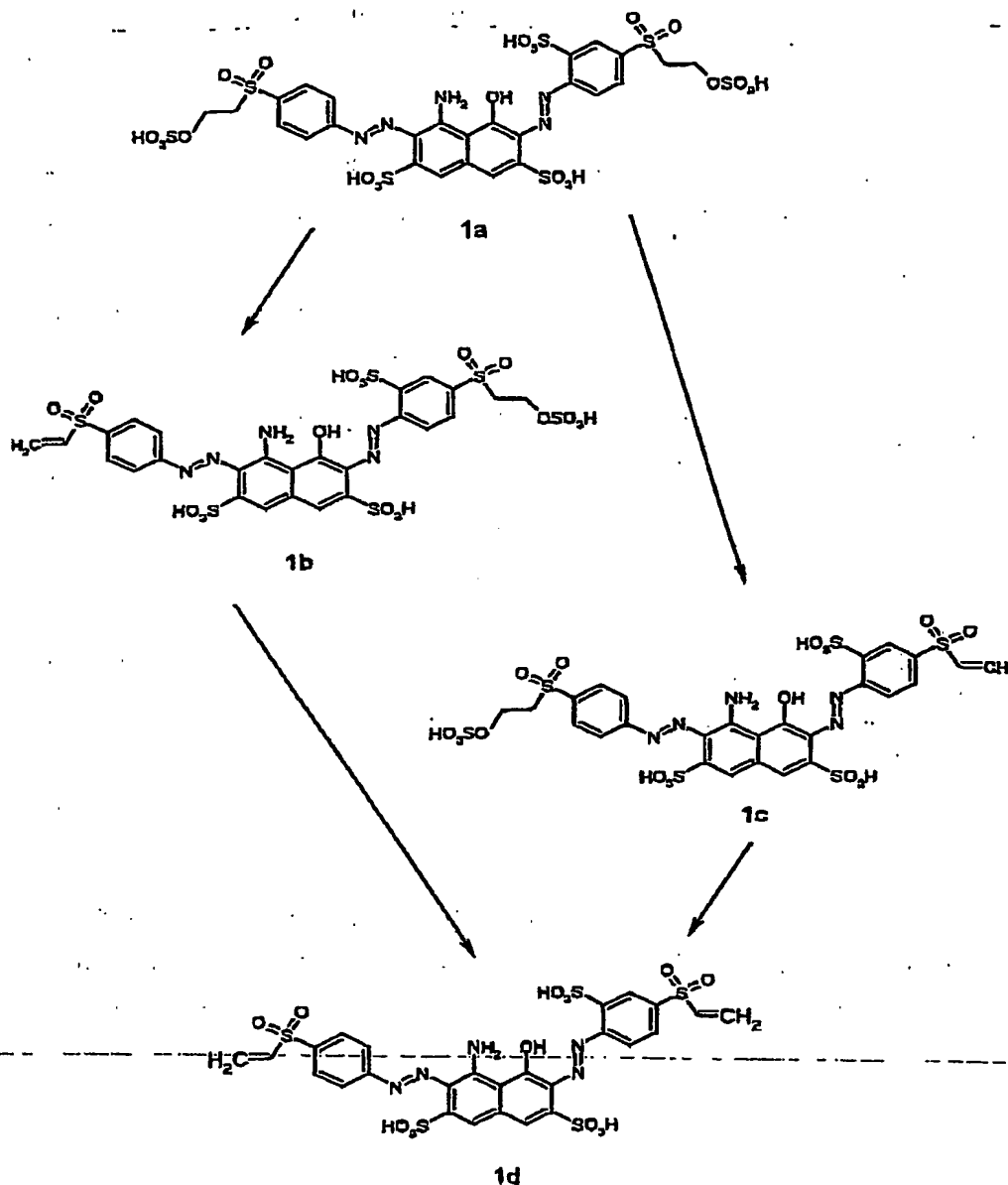
There are synthetic reasons why technical grades of the dye of the dye 1a will generally contain a 5-10% fraction of C.I. Reactive Black 5 (cf. formula 2a). Since the dye C.I. Reactive Black 5 has distinctly worse fastnesses than the dye 1a, the fraction of 2a (C.I. Reactive Black 5) should be minimized by suitable measures and it is for example advantageous in the synthesis of the dye of the formula 1a to keep the excess of the diazo component 4, which is customarily about 5-15% with regard to 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (5), to a minimum.



Treatment of the dye of the formula 1a with different amounts of a strong base such as an alkali metal hydroxide for example gives mixtures containing the dyes of the formulae 1a, 1b, 1c and 1d. The amount of base added is between 1.3 and 2.4 equivalents.

case 2002CH005 (corrected according to R 91.1 PCT)

8



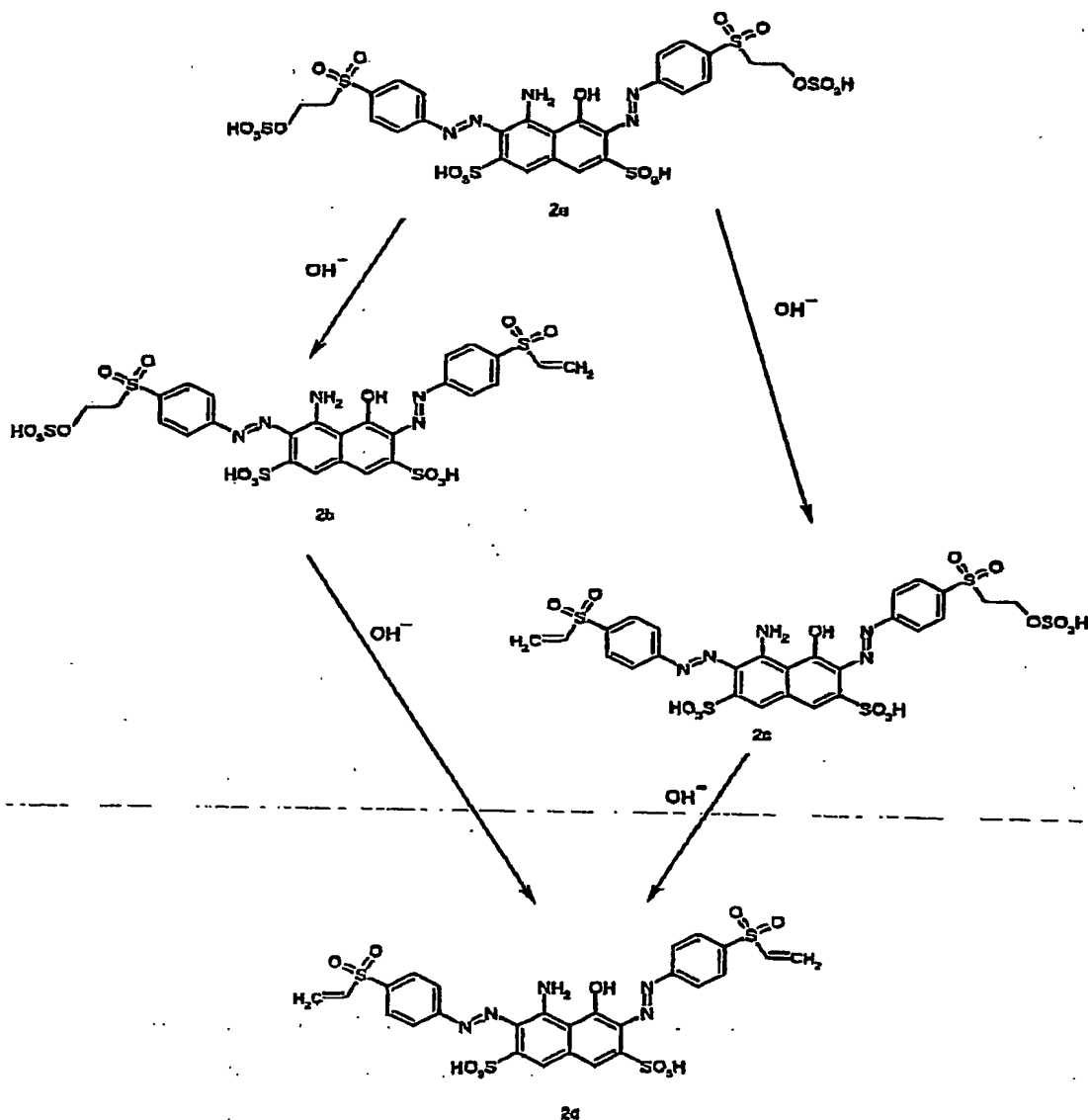
The mixtures produced by addition of 1.5–2 equivalents of a strong base such as sodium hydroxide contain the bis(vinyl sulphone) dye of the formula 1d as a main component.

- 5 Such mixtures exhibit distinctly increased affinity over the original dye 1a in the salt phase of an exhaust dyeing process (prior to the addition of alkali in the dyeing process). In addition, these dye mixtures are very suitable for trichromatic dyeings with yellow/orange and red/brown elements. Despite the distinctly increased affinity, the dye mixtures according to the invention still exhibit good solubilities.

case 2002CH005 (corrected according to R 91.1 PCT)

9

It will be appreciated that the dye 2a which may be present in the technical grade batches of the dye 1a will react with alkali in a similar manner to the dye 1a. An alkali treatment of the dye 2a gives rise to the dyes of the structures 2b, 2c and consequently to the dye of the structure 2d.

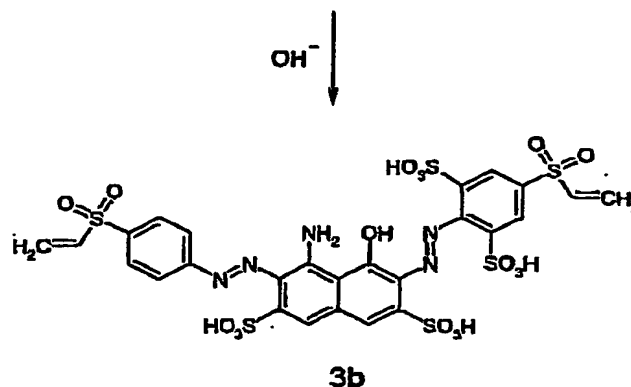
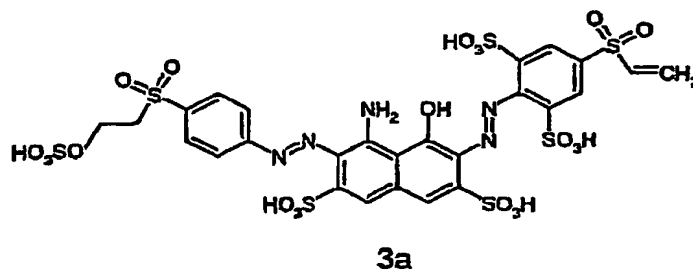


When 2-amino-5-(2'-sulphatoethylsulphonyl)benzenesulphonic acid is prepared by sulphonation of 4-aminophenyl 2'-sulphatoethyl sulphone, as described in the patent specification DE 2538723, the dyes of the structures 3a and 3b will likewise be

case 2002CH005 (corrected according to R 91.1 PCT)

10

detectable in small amounts in the reaction mixture.



- 5 The dye 1d according to the invention or mixtures of the dyes 1a, 1b, 1c and 1d are suitable for use as blue components for the trichromatic dyeing process.

Various red, brown, yellow and orange dyes are suitable together with the blue component of the formula 1.

10

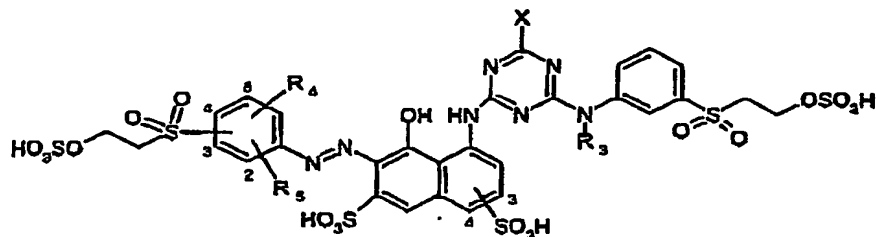
Preference is given to combinations containing compounds of the formula 1 or mixtures of compounds of the formula 1 and the fraction of the compound 1d in the mixtures as per formula 1 is more than 40% and at least one of the following compounds of the formula *ria*, *rib*, *ric*, *rid*, *rii*, *riii*, *riv*, *rv*, *gi*, *gii*, *giii*, *giv* or *gv*.

15

Preference for use as further components with the compounds of the formula 1 is given to red dyeing compounds of the formula *via*

case 2002CH005 (corrected according to R 91.1 PCT)

11



11a

where

the SO₂ group is in position 3, 4 or 5;

R₃ is a proton, methyl or ethyl;

5 R₄ is a proton, a sulpho group or an alkoxy group;

R₅ is a proton, an alkyl group or an alkoxy group; and

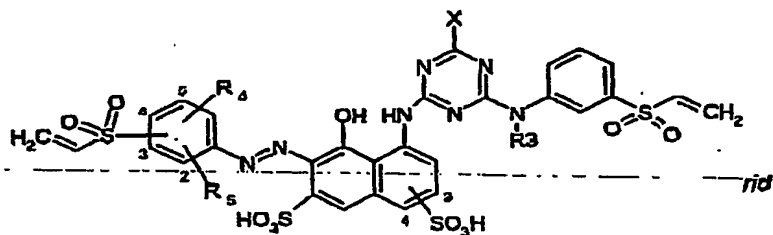
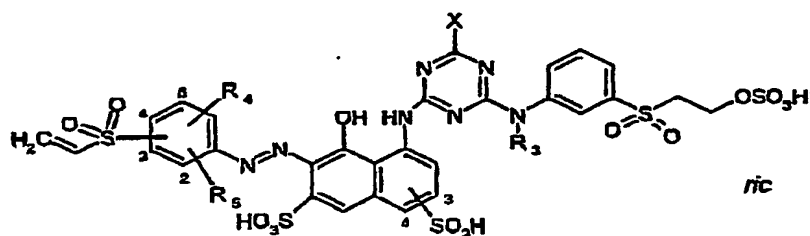
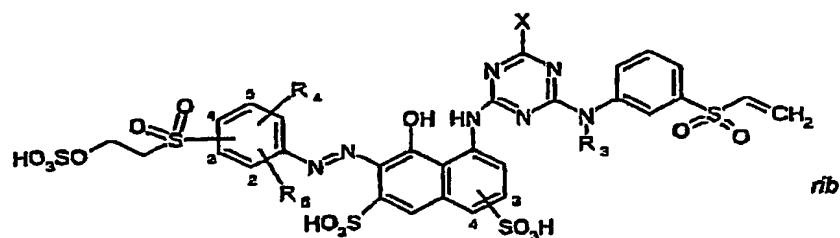
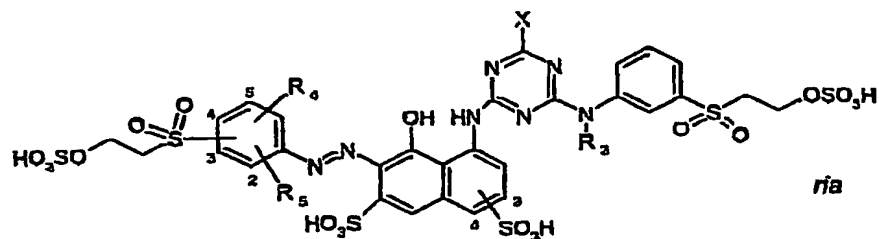
X is a halogen.

Preference for use as further components together with the compounds of the formula 1

10 is similarly given to mixtures of red dyes of the formula 11a, 11b, 11c and 11d

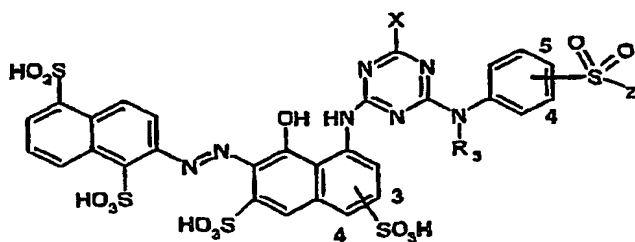
case 2002CH005 (corrected according to R 91.1 PCT)

12



where the substituents are each as defined above.

Preference for use as further components together with the compounds of the formula 1
5 is similarly given to red dyeing compounds of the formula *rii*.



case 2002CH005 (corrected according to R 91.1 PCT)

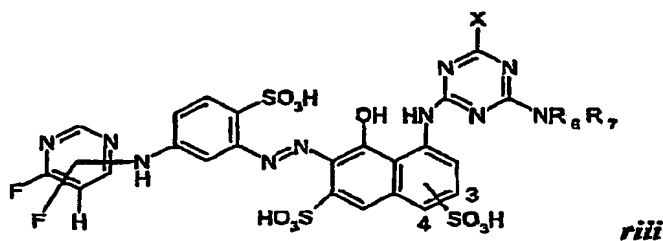
13

where the substituent R_3 is as defined above

and Z is $\text{CH}_2\text{CH}_2\text{Y}$ or $\text{CH}=\text{CH}_2$

Y is an alkali-detachable group, such as $-\text{OSO}_3\text{H}$, Cl

- 5 Preference for use as further components together with the compounds of the formula 1 is similarly given to red dyeing compounds of the formula *riii*



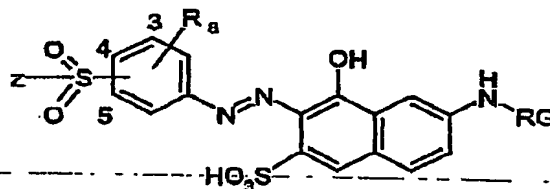
riii

where

the SO_3H group is in position 3 or 4

- 10 - NR_6R_7 is morpholine or $-\text{NHCH}_2\text{CH}_2\text{OH}$ and
X is a halogen.

Preference for use as further components together with the compounds of the formula 1 is similarly given to red dyeing compounds of the formula *riv*



riv

where

Z has the abovementioned meaning,

the SO_2 group is in position 3, 4 or 5;

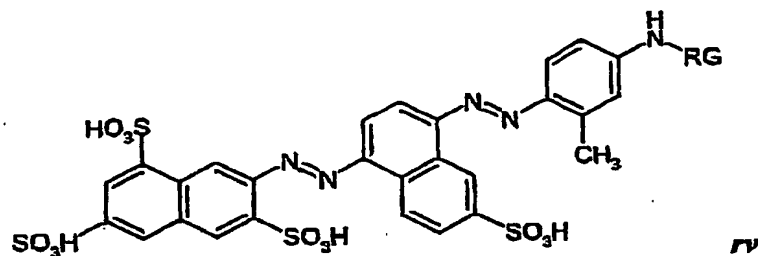
- 20 R_8 is a proton, a sulpho group or an alkoxy group and
RG is a heterocyclic reactive group, such as a difluoropyrimidyl or monofluorotriazinyl group

Preference for use as further components together with the compounds of the formula 1

- 25 is similarly given to brown dyeing compounds of the formula *rv*

case 2002CH005 (corrected according to R 91.1 PCT)

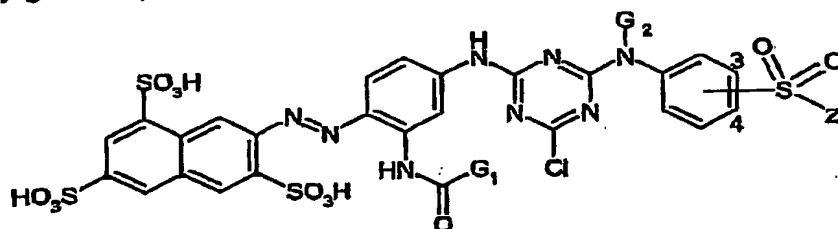
14



iv

where RG has the abovementioned meaning

- 5 Preference for use as further components together with the compounds of the formula 1 is similarly given to yellow dyeing compounds of the formula *gi*



gi

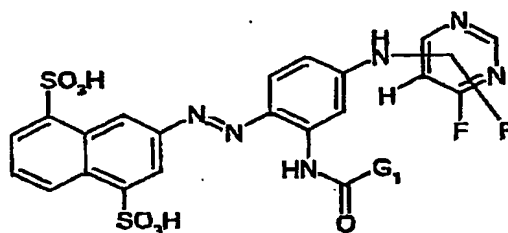
where Z has the abovementioned meaning

the SO₂ group is in position 3 or 4;

- 10 G₁ is NH₂ or CH₃,

G₂ is a proton, methyl or ethyl group;

Preference for use as further components together with the compounds of the formula 1 is similarly given to yellow dyeing compounds of the formula *gii*



gii

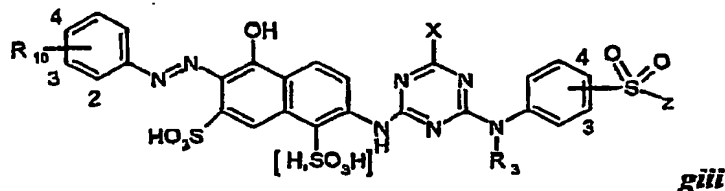
15

where G₁ has the abovementioned meaning

Preference for use as further components together with the compounds of the formula 1 is similarly given to orange dyeing compounds of the formula *giii*

case 2002CH005 (corrected according to R 91.1 PCT)

15



giii

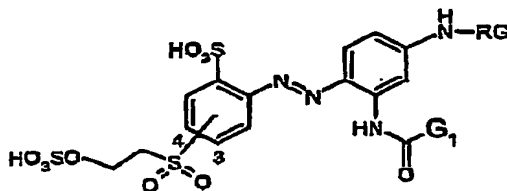
where

the substituents R_3 and Z have the abovementioned meanings,

the SO_2 group is in position 3 or 4;

5 R_{10} is in position 2, 3 or 4 and is an SO_3H , $COOH$, or SO_2Z group,

Preference for use as further components together with the compounds of the formula 1 is similarly given to yellow or orange dyeing compounds of the formula giv

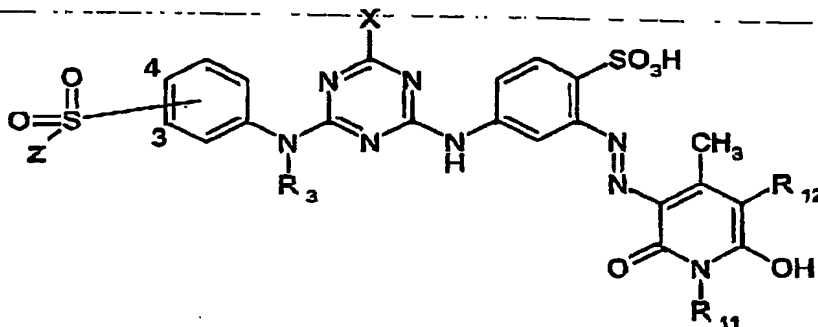


10

where G_1 and RG have the abovementioned meanings

Preference for use as further components together with the compounds of the formula 1 is similarly given to yellow dyeing compounds of the formula gv

15



where X , R_3 and Z have the abovementioned meanings

R_{11} is CH_3 , C_2H_5 or CH_2CH_2COOH ,

R_{12} is a proton, CN , $CONH_2$, $COOH$ or CH_2SO_3H

case 2002CH005 (corrected according to R 91.1 PCT)

16

Examples

Example 1

A dye mixture prepared according to the synthesis in Example 1 of the patent specification CH 657 865 A5, of the following composition:

5

about 90	parts	of the dye of the formula 1a,
about 5	parts	of the dye of the formula 1b,
about 4	parts	of the dye of the formula 1c and
about 1	part	of the dye of the formula 1d,

10

has the following composition following the addition of 1.5 equivalents of sodium hydroxide:

15

about 13	parts	of the dye of the formula 1a,
about 13.5	parts	of the dye of the formula 1b,
about 24.5	parts	of the dye of the formula 1c and
about 36	parts	of the dye of the formula 1d,

where the formulae 1a, 1b, 1c, 1d have the abovementioned meaning

20

Example 2

Reacting the dye mixture mentioned in Example 1 with 2 instead of 0.15 equivalents of sodium hydroxide affords a dye mixture of the following composition

25

about 0.5	part	of the dye of the formula 1a,
about 2.5	parts	of the dye of the formula 1b,
about 1.5	parts	of the dye of the formula 1c and
about 77	parts	of the dye of the formula 1d

30

where the formulae 1a, 1b, 1c, 1d have the abovementioned meaning

case 2002CH005 (corrected according to R 91.1 PCT)

17

Example 3

4-Aminophenyl 2'-sulphatoethyl sulphone is sulphonated as described in DE 2538723.

5 The sulphonation mixture is discharged onto ice, salted out and filtered off.

29.5 parts of 4-aminophenyl 2'-sulphatoethyl sulphone are diazotized and coupled under acid conditions onto 31.9 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid.

99 parts of the abovementioned, about 40% strength salted-out filtered-off, acidic (due
10 to sulphuric acid residues) sulphonation product (containing 39.7 parts of diazotizable amine) are diazotized and coupled at pH 5-7 onto the above-prepared reaction mixture of the acidic azo coupling of diazotized 4-aminophenyl 2'-sulphatoethyl sulphone onto 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid.

15 This gives a reaction solution which contains the following dyes:

	about 73	parts	of the dye of the formula 1a,
	4	parts	of the dye of the formula 1b,
	about 3	parts	of the dye of the formula 1c
20	about 10	parts	of the dye of the formula 2a
	about 1	part	of the dye of the formula 1d
	about 1	part	of the dye of the formula 2b or 2c
	about 5	parts	of the dye of the formula 3a

25 where the formulae 1a, 1b, 1c, 1d, 2a, 2b, 2c and 3a have the abovementioned meaning:

The reaction mixture is desalted by dialysis. The desalted reaction mixture is treated with 23.5 parts of concentrated sodium hydroxide solution at 15-25°C for 2-3 h.

30 The reaction solution thus treated is a mixture which contains the following components:

case 2002CH005 (corrected according to R 91.1 PCT)

18

- 5 about 0.5 part of the dye of the formula 1a,
about 2 parts of the dye of the formula 1b,
about 5 parts of the dye of the formula 1c
about 2 parts of the dye of the formula 2a
about 65 parts of the dye of the formula 1d
about 5 parts of the dye of the formula 2b or 2c
about 4 parts of the dye of the formula 3b,

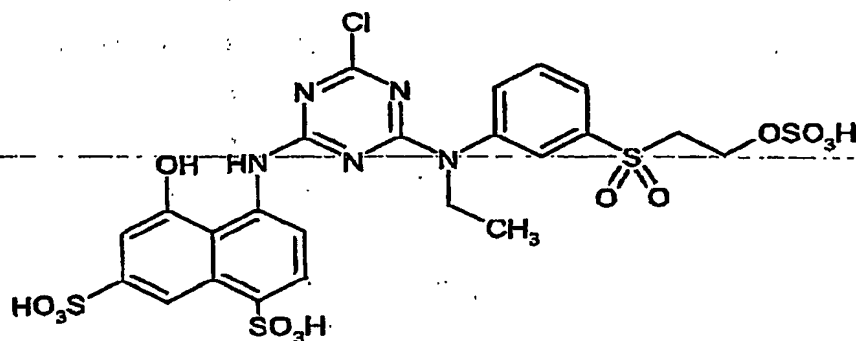
10 where the formulae 1a, 1b, 1c, 1d, 2a, 2b, 2c and 3b have the abovementioned meaning

The mixture obtained can be evaporated or directly used for dyeing.

Red and brown dyes

15 Example r1

The condensation product of 63.8 parts of 1-amino-8-hydroxynaphthalene-4,6-disulphonic acid and 37 parts of 2,4,6-trichlorotriazine is reacted with 70 parts of 3-ethylamino-phenyl 2'-sulphatoethyl sulphone of the following formula r1b:



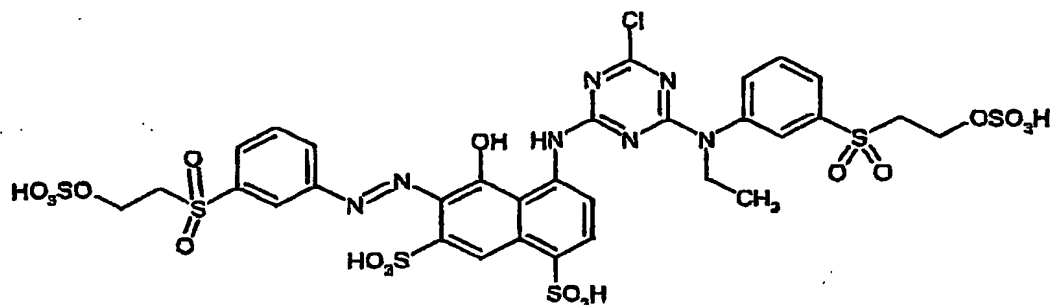
20

r1b

58 parts of 3-aminophenyl 2'-sulphatoethyl sulphone are diazotized and coupled at pH 5-5.5 onto the previously prepared coupling component r1b
The dye of the formula r1a

case 2002CH005 (corrected according to R 91.1 PCT)

19

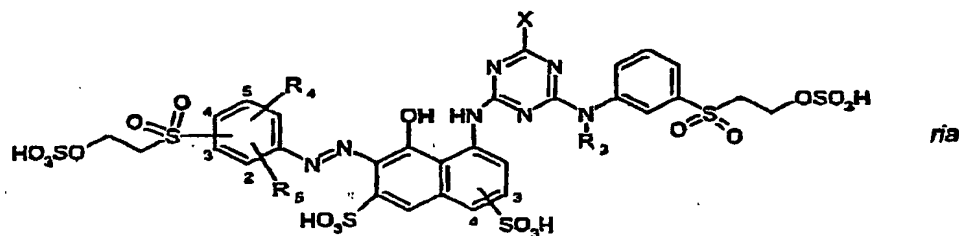


is salted out, filtered off and dried at 50°C under reduced pressure

The following Examples r2- r18 are prepared similarly to Example r1a.

5. Examples r2-r18

Examples r2-r18 of red dyeing compounds of the formula *ria*



Ex	-O ₂ S- position	-SO ₃ H position	R ₃	R ₄	R ₅	X
r2	3	3	-CH ₂ CH ₃	H	H	F
r3	4	3	-CH ₂ CH ₃	H	H	F
r4	4	3	-CH ₂ CH ₃	H	H	Cl
r5	4	4	-CH ₂ CH ₃	H	H	Cl
r6	4	4	-CH ₂ CH ₃	H	H	F
r7	4	3	-CH ₃	H	H	F
r8	3	3	-CH ₃	H	H	F
r9	5	3	-CH ₂ CH ₃	(2)-OCH ₃	H	Cl
r10	4	3	-CH ₂ CH ₃	(2)-OCH ₃	(5)-CH ₃	Cl
r11	4	3	-CH ₃	(2)-OCH ₃	(5)-OCH ₃	F
r12	4	4	-CH ₂ CH ₃	(2)-OCH ₃	(5)-OCH ₃	Cl

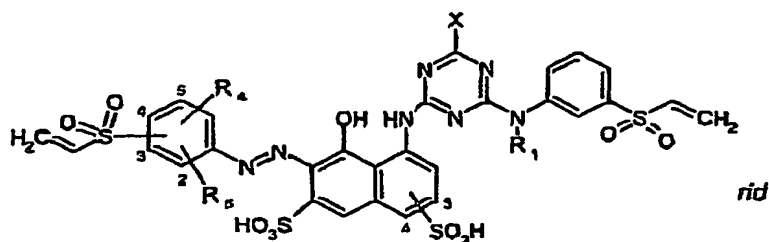
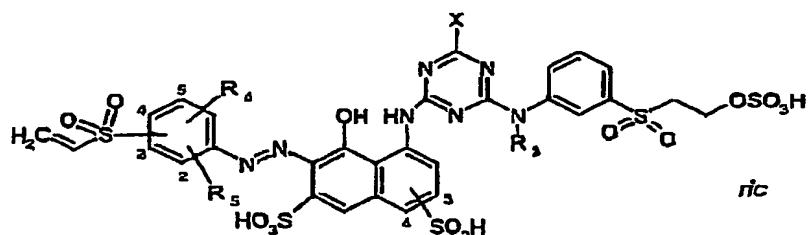
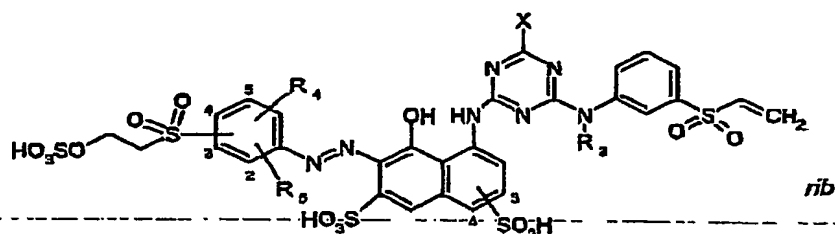
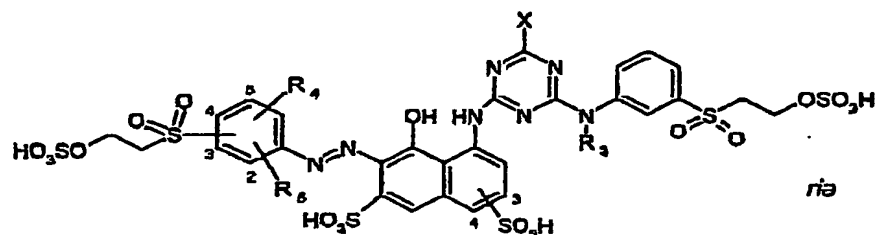
case 2002CH005 (corrected according to R 91.1 PCT)

20

r13	4	4	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r14	5	3	-CH ₃	(2)-SO ₃ H	H	F
r15	5	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r16	4	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r17	4	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	F
r18	3	3	-CH ₂ CH ₃	(4)-OCH ₃	H	Cl

Reacting dyes of the formula ri at room temperature with 1 equivalent of aqueous sodium hydroxide solution affords mixtures of red dyes of the formula (ria), (rib), (ric) and (rid).

5

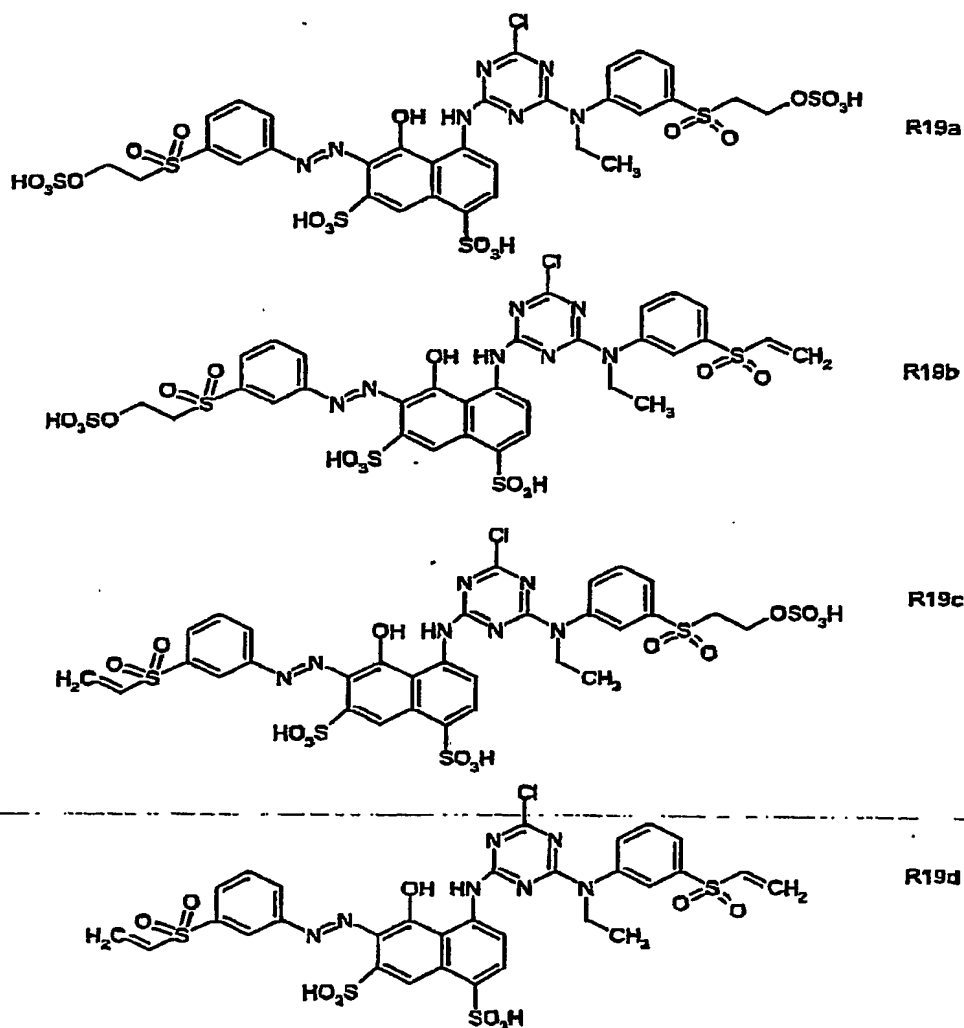


case 2002CH005 (corrected according to R 91.1 PCT)

21

Example r19. Reacting a solution of the dye of the formula r1a with 1 equivalent of aqueous sodium hydroxide solution affords a dye mixture of the formulae r19a, r19b, r19c, r19d which is salted out, filtered off and dried at 50°C under reduced pressure.

5



Examples r20-r35 can be prepared similarly to Example r19 by alkali treatment of Examples r2-r18 (compare formulae *ria*, *rib*, *ric* and *rid*).

case 2002CH005 (corrected according to R 91.1 PCT)

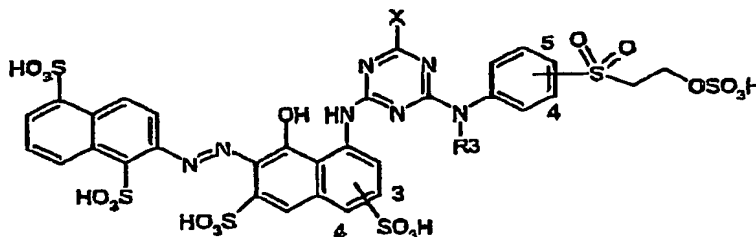
22

Ex	-O ₂ S- position	-SO ₃ H position	R ₃	R ₄	R ₅	X
r20	3	3	-CH ₂ CH ₃	H	H	F
r21	4	3	-CH ₂ CH ₃	H	H	F
r22	4	3	-CH ₂ CH ₃	H	H	Cl
r23	4	4	-CH ₂ CH ₃	H	H	Cl
r24	4	4	-CH ₂ CH ₃	H	H	F
r25	4	3	-CH ₃	H	H	F
r26	3	3	-CH ₃	H	H	F
r27	5	3	-CH ₂ CH ₃	(2)-OCH ₃	H	Cl
r28	4	3	-CH ₂ CH ₃	(2)-OCH ₃	(5)-CH ₃	Cl
r29	4	3	-CH ₃	(2)-OCH ₃	(5)-OCH ₃	F
r30	4	4	-CH ₂ CH ₃	(2)-OCH ₃	(5)-OCH ₃	Cl
r31	4	4	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r32	5	3	-CH ₃	(2)-SO ₃ H	H	F
r33	5	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r34	4	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	Cl
r35	4	3	-CH ₂ CH ₃	(2)-SO ₃ H	H	F

Example r36-r41

Examples r36-r41 can be prepared similarly to Example r1 by replacing 3-aminophenyl
 5 2'-sulphatoethyl sulphone by 2-naphthylamine-1,5-disulphonic acid.

Examples of red dyeing compounds of the formula *riia*

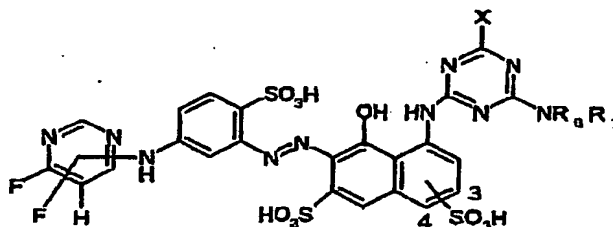


case 2002CH005 (corrected according to R 91.1 PCT)

23

Ex	-O ₂ S- position	-SO ₃ H position	R ₃	X
r36	4	3	-CH ₂ CH ₃	Cl
r37	4	3	-CH ₂ CH ₃	Cl
r38	4	3	H	Cl
r39	3	4	-CH ₂ CH ₃	Cl
r40	3	3	-CH ₂ CH ₃	Cl
r41	3	3	H	Cl

Examples r42-r44

Examples of red dyeing compounds of the formula *iii*

5

Ex	-SO ₃ H position	-NR ₆ R ₇	X
r42	3		F
r43	3		Cl
r44	4	-NHCH ₂ CH ₂ OH	Cl

The dye r42 is described in EP525572. By changing the coupling component in the azo coupling reaction, the two examples r43 and r44 can be prepared similarly.

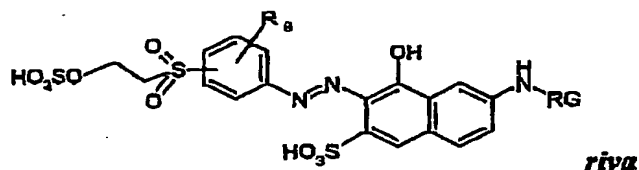
case 2002CH005 (corrected according to R 91.1 PCT)

24

Example r45

58 parts of 4-aminophenyl 2'-sulphatoethyl sulphone are diazotized and coupled at pH 6-7 onto the condensation product of 47.8 parts of 2-amino-8-hydroxynaphthalene-6-sulphonic acid and 28 parts of 2,4,6-trifluoropyrimidine. The dye conforming to formula R45 is salted out, filtered off and dried.

Examples of red dyeing compounds of the formula *riva*

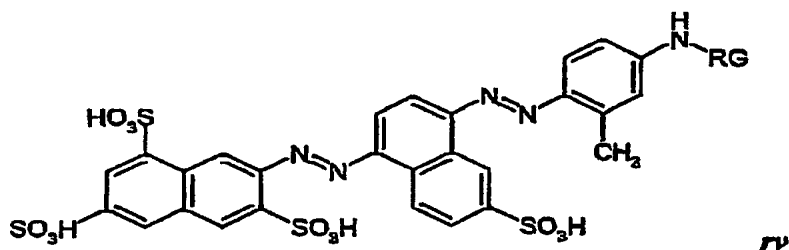


10

Ex	-SO ₂ - position	R ₉	RG
r45	4	H	

case 2002CH005 (corrected according to R 91.1 PCT)

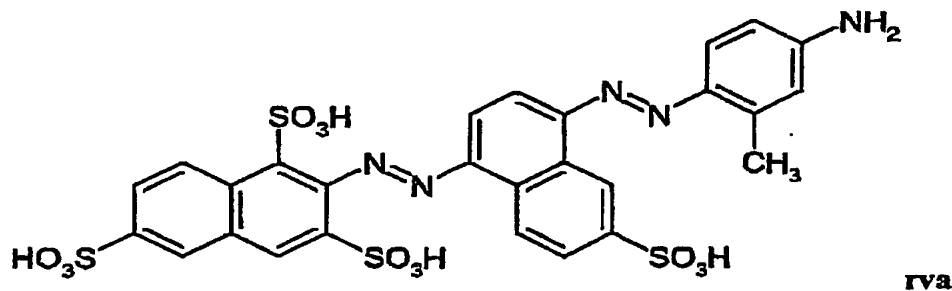
25

Examples r46-r47Examples of brown dyeing compounds of the formula *rv*

5

Ex	RG
r46	
r47	

The brown dye **r46** is prepared by condensation of 32 parts of 2,4,6-trifluoropyrimidine with 147 parts of the amino chromophore of the formula *rva*.



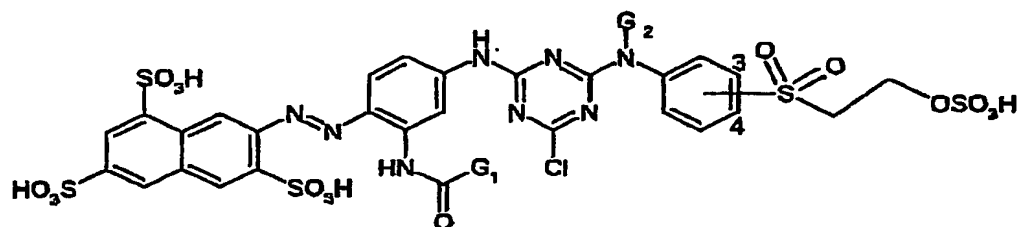
- 10 Replacing the 32 parts of 2,4,6-trifluoropyrimidine by 100 parts of a condensation product of 2,4,6-trichlorotriazine with 3-ethylaminophenyl 2'-sulphatoethyl sulphone affords the brown dye of the formula **r47**

case 2002CH005 (corrected according to R 91.1 PCT)

26

Yellow or orange dyes

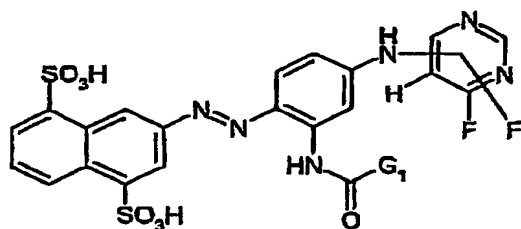
Examples g1-g4

Examples of yellow dyeing compounds of the formula *gia**gi*

5

Ex	-O ₂ S- position	G ₁	G ₂
g1	4	NH ₂	H
g2	3	NH ₂	H
g3	4	CH ₃	-CH ₂ CH ₃
g4	4	CH ₃	H

Examples g5-g6

Examples of yellow dyeing compounds of the formula *gii**gii*

10

The dye of the formula g5 was described in Lehr, F. "Synthesis and application of reactive dyes with heterocyclic reactive systems" Dyes Pigm. (1990), 14(4), 239-63.

The dye of the formula g6 can be prepared in a similar manner.

15

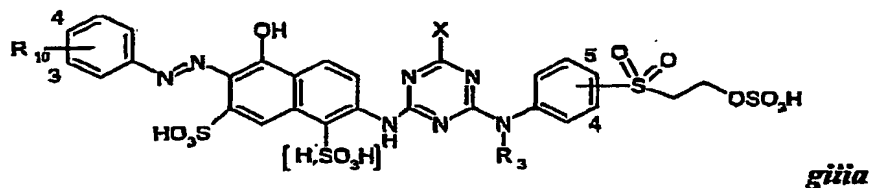
case 2002CH005 (corrected according to R 91.1 PCT)

27

Ex	G1
g5	CH ₃
g6	NH ₂

Examples g7-g11

Examples of orange dyeing compounds of the formula *giii*. Examples g7-g11 can be prepared similarly to Example r1.

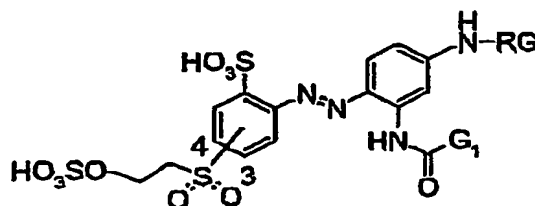


5

Ex.	R ₁₀ (Pos.)	H, SO ₃ H	R ₃	X	-SO ₂ - pos
g7	CH ₂ CH ₂ OSO ₃ H (4)	SO ₃ H	CH ₂ CH ₃	Cl	3
g8	CH ₂ CH ₂ OSO ₃ H (4)	SO ₃ H	CH ₂ CH ₃	Cl	4
g9	SO ₃ H (4)	H	H	Cl	4
g10	SO ₃ H (4)	H	CH ₂ CH ₃	Cl	3
g11	SO ₃ H (3)	H	H	Cl	4

Examples g12-g14

Examples of yellow or orange dyeing compounds of the formula *giva*.

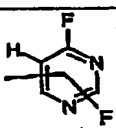
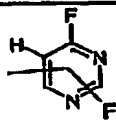
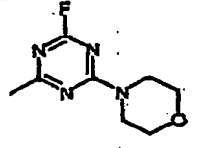


10

The preparation of Examples g12-g14 is evident from the German patent application DE 4425222 A1 or WO 9602593 A1

case 2002CH005 (corrected according to R 91.1 PCT)

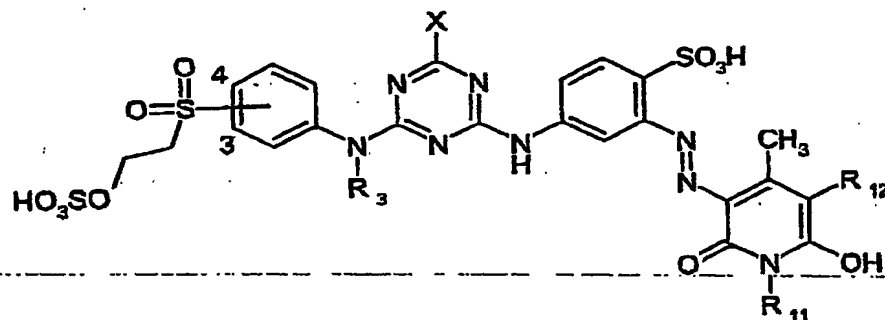
28

Ex.	-SO ₂ CH ₂ CH ₂ OSO ₃ H position	G1	RG'
g12	4	-NH ₂	
g13	3	-CH ₃	
g14	4	-NH ₂	

Examples g15-g17

Examples of yellow dyeing compounds of the formula *gva*

5

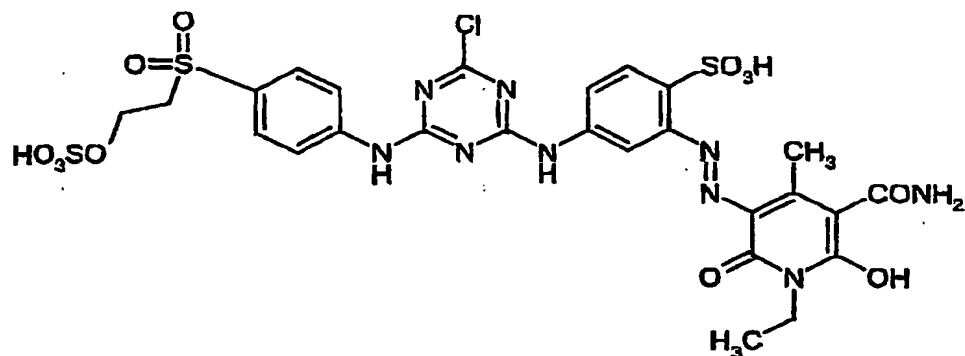


Example g15

10 The condensation product of 58 parts of 3-aminophenyl 2'-sulphatoethyl sulphone and 37 parts of 2,4,6-trichlorotriazine is reacted with 38 parts of 2,4-diaminobenzenesulphonic acid. The intermediate formed is diazotized and coupled onto 38 parts of 1-ethyl-5-carbamoyl-6-hydroxy-4-methyl-2-pyridone. The resulting dye conforms to the formula g15

case 2002CH005 (corrected according to R 91.1 PCT)

29



g15

g16-g17

Examples g16 and g17 can be prepared in a similar fashion

Ex	-O ₂ S- position	R ₃	R ₁₁	R ₁₂	X
g16	3	-CH ₂ CH ₃	-CH ₂ CH ₂ COOH	-CONH ₂	Cl
g17	4	H	-CH ₂ CH ₂ COOH	-CONH ₂	Cl

5

Use examples of trichromatic dyeings

A 20 g sample of a bleached cotton tricot is introduced at 60°C into a solution of 16 g of sodium sulphate and

10

0.5% (on weight of fibre) of the navy dye mixture as per Example 2.

0.8% of a yellow dye as per Example g2

0.5% of a red dye as per Example r22

in 200 ml of water

15

At 60°C, portions of 0.3, 0.7 and 1 g of sodium carbonate are added after 30, 45 and 60 minutes respectively. The temperature is kept constant for a further 30 minutes.

Thereafter, the dyed fabric is rinsed for 2 minutes with hot deionized water and for one minute in hot tap water. After boiling out in 1 000 ml of deionized water for 20 minutes,

20

the tricot is dried. The result is a brown cotton dyeing having excellent fastnesses.

case 2002CH005 (corrected according to R 91.1 PCT)

30

Use Examples 2-8

These examples are carried out similarly to Use Example 1, except for the use of the hereinbelow recited dye mixtures.

5

Use Example 2 (olive dyeing)

0.6% of the navy dye mixture as per Example 3
0.4% of a yellow dye as of Example g1
0.2% of a red dye as of Example r38

10

Use Example 3 (brown dyeing)

0.6% of the navy dye mixture as per Example 2
0.9% of an orange dye as of Example g9
0.3% of a red dye as of Example r45

15

Use Example 4 (olive dyeing)

0.6% of the navy dye mixture as per Example 3
0.1% of a yellow dye as of Example g5
0.1% of a red dye as of Example r42

20

Use Example 5 (brown dyeing)

0.3% of the navy dye mixture as per Example 3
0.9% of a yellow dye as of Example g2
0.5% of a red dye as of Example r38

25

Use Example 6 (olive dyeing)

0.3% of the navy dye mixture as per Example 3
0.4% of an orange dye as of Example g7
0.2% of a red dye as of Example r38

30

Use Example 7 (olive dyeing)

0.6% of the navy dye mixture as per Example 2
0.4% of a yellow dye as of Example g12

16-04-2004

IB0302396

06/04 '04 DI 19:23 FAX 0041 61 4696588

CLARIANT PATENTS

+++ EP PAT MÜNCHEN

040

case 2002CH005 (corrected according to R 91.1 PCT)

31

0.2% of a red dye as of Example r22

Use Example 8 (brown dyeing)

0.3 % of the navy dye mixture as per Example 3

5 0.9% of a yellow dye as of Example g16

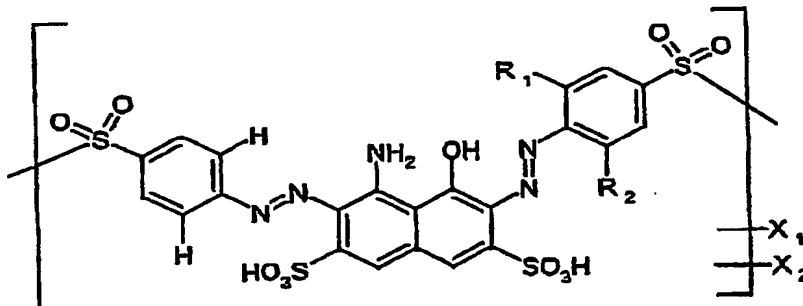
0.5% of a red dye as of Example r38

case 2002CH005 (corrected according to R 91.1 PCT)

32

Claims

1. Mixtures containing compounds of formula 1



1

- or mixtures of compounds of formula 1
where

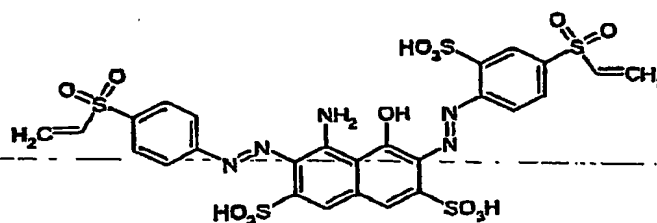
R_1 is H, SO_3H ,

R_2 is H, SO_3H

X_1 is $CH=CH_2$, $CH_2CH_2OSO_3H$

X_2 is $CH=CH_2$, $CH_2CH_2OSO_3H$,

characterized in that the fraction of the compound 1d



1d

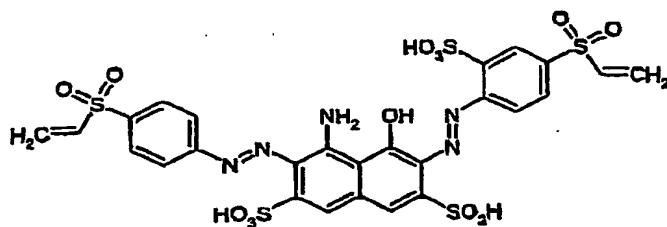
- in the mixtures as per formula 1 is more than 40%.

2. Mixtures as per Claim 1 characterized in that the mixture of the compounds as per formula 1 comprises more than 50% of the compound as per formula 1d

20

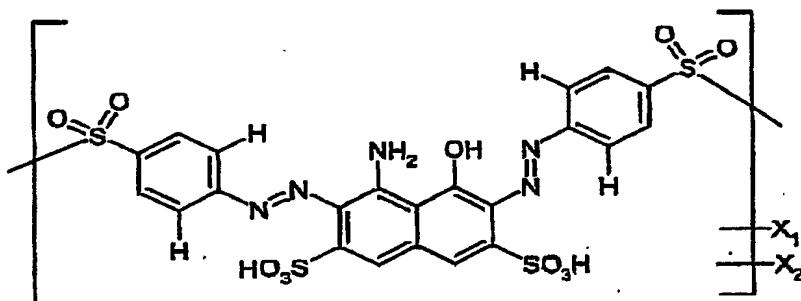
case 2002CH005 (corrected according to R 91.1 PCT)

33



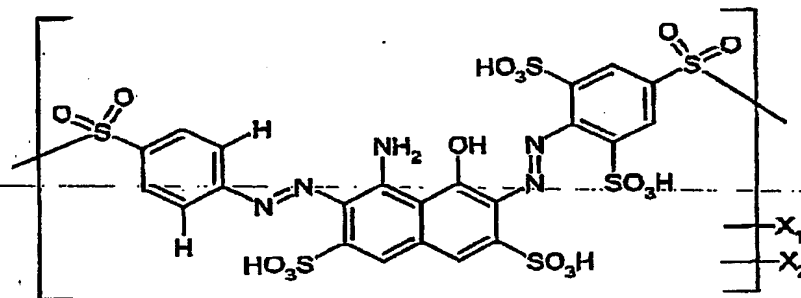
1d

and less than 20% of the compound as per formula 2



2

and less than 10% of the compound as per formula 3



3

10

where

R₁ is H, SO₃H,R₂ is H, SO₃HX₁ is CH=CH₂, CH₂CH₂OSO₃HX₂ is CH=CH₂, CH₂CH₂OSO₃H.

15

6-04-2004

IB0302396

06/04 '04 DI 19:23 FAX 0041 61 4696588

CLARIANT PATENTS

EP PAT MÜNCHEN

043

case 2002CH005 (corrected according to R 91.1 PCT)

34

3. Use of mixtures according to Claims 1 or 2 as a blue component in the trichromatic dyeing process.
4. Ink jet printing inks comprising mixtures according to Claims 1 or 2.
5. Process for printing or dyeing hydroxyl- or nitrogen-containing organic substrates characterized in that mixtures according to Claims 1 or 2 are used.
6. Hydroxyl- or nitrogen-containing organic substrates characterized in that they have been printed or dyed with mixtures according to Claims 1 or 2.

10